CENTRIFUGAL DISTORTION OF AXIAL MOLECULES AND THE POTENTIAL FUNCTIONS OF THE METHYL HALIDES

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ZAKA I. SLAWSKY

A THESIS

Submitted in Partial Fulfillment of the Requirements
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The Centrifugal Distortion of Axial Molecules

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University of Michigan, Ann Arbor, Michigan
(Received May 1, 1939)

The theory of the semi-rigid rotator developed by Wilson and Howard has been applied to the axial molecules YX_3 and ZYX_3. It is found that the change in rotational energy, δW, caused by the centrifugal distortion, can be expressed in terms of the quantum numbers J and K and as a function of the potential constants and the molecular dimensions. The formula is evaluated explicitly for NH_3, and ND_3, and for the former is, in cm^{-1}:

$$\frac{\delta W_{JK}}{hC} = -0.000625J^2(J+1)^2+0.000950K^2J(J+1) +0.000799J(J+1)-0.000630K^4-0.00189K^2.$$

The pure rotation lines of NH_3 and of ND_3 are calculated and compared with the observations of Wright and Randall, and of Barnes. The agreement is very satisfactory. The theory predicts that the rotation lines are multiple. The spacing of this fine structure was too small to be observable in the region mapped by Wright and Randall but should be possible to detect in the case of the higher members of the rotation series.

We have also calculated the pure rotation spectrum of PH_3 by using Howard's approximate values of the dimensions and force constants of this molecule. The agreement with experimental values is as good as could be expected from such rough data.

RECENTLY two interesting papers by Wilson and Howard[1] and by Wilson[2] have appeared which deal with the vibration rotation energy levels of polyatomic molecules. In these papers there is developed, along general lines, the effect of the centrifugal force stretching upon the

[1] E. B. Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).
[2] E. B. Wilson, J. Chem. Phys. **4**, 313 (1936).

rotational levels. The experimental existence of such an effect has been observed in the far infrared for NH_3 and PH_3 by Wright and Randall[3] who found that the pure rotation lines of these molecules are not linearly spaced—as must be expected for a rigid rotator—but that their positions are given by a formula of the type: $\nu = AJ - BJ^3$. The constant B is very small, indicating that the centrifugal force stretching, although clearly observable, is a higher order effect. Similar observations have been made by Barnes[4] on ND_3 and have been confirmed for the molecule NH_3 by the measurements of Houston[5] on the Raman spectrum of that molecule.

We propose to apply the theory developed by Wilson and Howard to tetratomic and pentatomic axial molecules and to obtain explicit expressions for the change in the rotational energy. We shall show that these expressions are in very good agreement with the available experimental data.

Howard and Wilson have derived a general expression for the Hamiltonian of a semi-rigid polyatomic molecule which is rather complicated. However, they show that if one is interested only in the rotational distortion of the nonvibrating molecule, the expression may be considerably simplified. Under these circumstances the energy, which is purely rotational and therefore suitable for calculating the pure rotation spectrum, takes the form,

$$W_R = \tfrac{1}{2}\sum_{\alpha\beta} \mu_{\alpha\beta}^{(0)} P_\alpha P_\beta - \tfrac{1}{8} \sum_{\alpha\beta\gamma\delta k} \frac{\mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)}}{\lambda_k} P_\alpha P_\beta P_\gamma P_\delta. \quad (1)$$

The indices α, β, γ, δ represent the directions in a rotating system of rectangular coordinates x, y, z, which will be defined in the next paragraph. The P's are matrices giving the components of the total angular momentum of the molecule along the coordinate axes. The index k denotes a normal mode of vibration and λ_k is connected to the normal frequency of vibration in the usual way, $\lambda_k = 4\pi^2 \nu_k^2$.

The $\mu_{\alpha\beta}^{(k)}$ are determined by the moments and products of inertia. Consider a rotating coordinate system whose origin is fixed at the center of gravity of the molecule, and whose axes are defined by the conditions that the angular momentum of the molecule with respect to them shall be zero at all times. The moments and products of inertia A, B, C, D, E and F relative to these axes are now calculated. Since the molecule is only semi-rigid, they will evidently be functions of the mutual displacements of the particles as well as of the equilibrium distances. It is convenient to express them in terms of the normal coordinates which are designated by $Q_1 \cdots Q_n$. A determinant is now built from the moments and products of inertia.

$$\Delta = \begin{vmatrix} A & -D & -F \\ -D & B & -E \\ -F & -E & C \end{vmatrix}$$

$\mu_{\alpha\beta}$ is the $\alpha\beta$ cofactor of Δ divided by Δ itself. $\mu_{\alpha\beta}^{(0)}$ is its equilibrium value, that is, $\mu_{\alpha\beta}$ in which the normal coordinates $Q_1 \cdots Q_n$ have all been set equal to zero. Thus the first term of Eq. (1) is the familiar expression for the rotational energy of a rigid molecule. The first derivative of $\mu_{\alpha\beta}$ with respect to Q_k evaluated at the equilibrium position is given the symbol $\mu_{\alpha\beta}^{(k)}$.

From the dimensions of the molecule we shall calculate the $\mu_{\alpha\beta}^{(k)}$ which are of course constants; then find a representation for the P's which satisfy the exchange rules but which in general will not make W diagonal. The final step will be to diagonalize W and thus obtain the eigenvalues of our problem.

The Axial Molecule YX_3

Consider the molecule YX_3. The geometrical configuration is such that the atoms occupy the corners of a regular pyramid, the Y atom at its vertex and the three X atoms at the corners of the equilateral triangular base. See Fig. 1.

The moments of inertia A, B and C and the products of inertia D, E and F of such molecules, may be readily calculated to the approximation in which only first powers in the displacements of the atoms from their equilibrium positions are retained.

[3] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).
[4] R. B. Barnes, Phys. Rev. **47**, 658 (1935).
[5] W. V. Houston, Phys. Rev. **44**, 903 (1933).

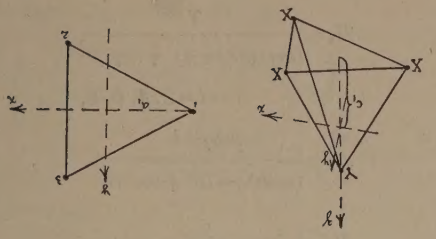

FIG. 1.

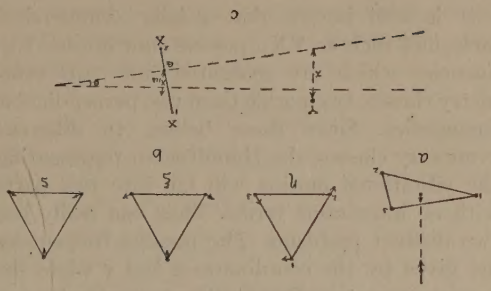

FIG. 2.

$$A = A_0 - 2mc_1(z_1+z_2+z_3-3z_4) - ma_1\sqrt{3}(y_2-y_3),$$

$$B = B_0 - 2mc_1(z_1+z_2+z_3-3z_4) - ma_1(2x_1-x_2-x_3),$$

$$C = C_0 - ma_1\sqrt{3}(y_2-y_3) - ma_1(2x_1-x_2-x_3),$$

$$D = -\tfrac{1}{2}ma(2y_1-y_2-y_3) - \frac{\sqrt{3}}{2}ma_1(x_2-x_3),$$

$$E = -mc_1(y_1+y_2+y_3-3y_4) - \frac{\sqrt{3}}{2}ma_1(z_2-z_3),$$

$$F = -mc_1(x_1+x_2+x_3-3x_4) - \tfrac{1}{2}ma_1(2z_1-z_2-z_3).$$

The coordinates x_1, x_2, x_3, and x_4 are the displacements from the equilibrium positions along the x direction of the three X atoms and the Y atom, respectively; y_1, y_2, y_3, and y_4 are similar displacements in the y direction and z_1, z_2, z_3, and z_4 along the z direction. A_0 and C_0 are the equilibrium values of the moments of inertia. A_0 is the moment of inertia about an axis through the center of gravity of the molecule and perpendicular to the geometrical axis of symmetry. C_0 is the moment of inertia about this axis of symmetry. c_1 is the distance of the center of gravity of the molecule from the plane of the X atoms, a_1 is the distance of the X atoms from the symmetry axis. m is the mass of an X atom.

These expressions may be considerably simplified when the symmetry of the molecule and the conservation of linear and angular momenta are taken into account. A coordinate system which does this will now be introduced. That one needs only six coordinates is evident from the fact that the YX_3 molecule has twelve degrees of freedom, three of which belong to the translation of the molecule, and three to its rotation. Hence only six coordinates are necessary for the six internal degrees of freedom of the molecule. The six coordinates we shall use are illustrated in Fig. 2. The coordinate z gives the displacement of the Y atom with respect to the center of gravity of the X atoms, which takes place along the geometrical axis of symmetry. The coordinates x or y measure the displacement of the Y atom from a line drawn perpendicular to the plane of the X atoms and through their center of gravity. The angle θ, which describes the tipping of the base with respect to the Y atom, is determined by the conservation of angular momentum, say about an axis through the center of gravity of the X atoms and perpendicular to the plane of the paper in Fig. 2c. The coordinates ξ, η and ζ are indicated in Fig. 2b. They are so chosen that the actual displacements are given by $\xi/\sqrt{3}$, $\eta/\sqrt{3}$ and $\zeta/\sqrt{3}$. Four of these coordinates x, y, ξ, η are the same as those used by Johnston and Dennison[6] and are discussed in their paper.

In terms of the six coordinates thus introduced, A, B, C, D, E and F assume a simpler form.

$$A = A_0 + 6mc_1z + \sqrt{3}ma_1(\zeta+\xi),$$

$$B = B_0 + 6mc_1z + \sqrt{3}ma_1(\zeta-\xi),$$

$$C = C_0 + 2\sqrt{3}ma_1\zeta,$$

$$D = \sqrt{3}ma_1\eta,$$

$$E = 6mc_1(C_0/2A_0)y,$$

$$F = 6mc_1(C_0/2A_0)x.$$

To introduce normal coordinates it is necessary to set up the usual determinant of the coefficients in the potential and kinetic energies of the molecule.

[6] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

It is well known that axially symmetrical molecules such as YX_3, possess four normal frequencies which are separated into two symmetry classes, two parallel and two perpendicular frequencies. Since these belong to different symmetry classes, the Hamiltonian representing the vibrational motion will fall into two parts with no interaction terms. Thus one really has two distinct problems. The parallel frequencies are given by the coordinates z and ζ while the motions corresponding to the perpendicular frequencies are given by x, y, ξ and η. The kinetic and potential energies are then

$$2T_{\shortparallel}=\mu\dot{z}^2+m\dot{\zeta}^2,$$

$$2V_{\shortparallel}=az^2+b\zeta^2+2cz\zeta,$$

$$2T_{\perp}=m\kappa(\dot{x}^2+\dot{y}^2)+m(\dot{\xi}^2+\dot{\eta}),$$

$$2V_{\perp}=\alpha(x^2+y^2)+\beta(\xi^2+\eta^2)+2\gamma(x\xi+y\eta),$$

where

$$\mu=\frac{3mM}{3m+M} \quad \text{and} \quad \kappa=\frac{C_0}{2A_0}\frac{\mu}{m};$$

a, b, c, α, β and γ are the potential constants.

The determinants which, when set equal to zero, yield the normal frequencies are

$$\begin{vmatrix} \mu\lambda-a & -c \\ -c & m\lambda-b \end{vmatrix}=0, \qquad \begin{vmatrix} m\kappa\lambda-\alpha & -\gamma \\ -\gamma & m\lambda-\beta \end{vmatrix}=0.$$

The first gives the parallel frequencies and the second, the doubly degenerate perpendicular frequencies. The relations between x, y, z, ξ, η, ζ and the normal coordinates Q_1, Q_2, Q_3, Q_4, Q_6 and Q_8 follow immediately,

$$x=A_2Q_2+A_4Q_4, \quad \xi=B_2Q_2+B_4Q_4,$$

$$y=A_6Q_6+A_8Q_8, \quad \eta=B_6Q_6+B_8Q_8,$$

$$z=A_1Q_1+A_3Q_3, \quad \zeta=B_1Q_1+B_3Q_3.$$

The subscripts are so chosen that the odd ones correspond to the parallel frequencies while the even subscripts belong to the perpendicular frequencies. The coefficients in these transformation equations are the normalized cofactors of the determinants.

$$A_i=\frac{m\lambda_i-\beta}{(m\kappa(m\lambda_i-\beta)^2+m\gamma^2)^{\frac{1}{2}}},$$

$$B_i=\frac{\gamma}{(m\kappa(m\lambda_i-\beta)^2+m\gamma^2)^{\frac{1}{2}}},$$

$$i=2, 4, 6, 8,$$

$$A_j=\frac{m\lambda_j-b}{(\mu(m\lambda_j-b)^2+mc^2)^{\frac{1}{2}}},$$

$$B_j=\frac{c}{(\mu(m\lambda_j-b)^2+mc^2)^{\frac{1}{2}}},$$

$$j=1, 3.$$

Inasmuch as the motions of the atoms in the plane perpendicular to the axis of symmetry are degenerate, $A_2=A_6$, $A_4=A_8$, $B_2=B_6$ and $B_4=B_8$.

The moments and products of inertia A, B, C, D, E and F may now be written in terms of the normal coordinates and the determinant Δ set up. Since all powers of the displacements above the first are rejected in our calculations, the determinant and all its cofactors may be readily expanded and the $\mu_{\alpha\beta}^{(k)}$ evaluated. If the coefficients of the matrices $P_\alpha P_\beta P_\gamma P_\delta$ are designated by $\tau_{\alpha\beta\gamma\delta}$, that is,

$$\tau_{\alpha\beta\gamma\delta}\equiv\sum_k\frac{\mu_{\alpha\beta}^{(k)}\mu_{\gamma\delta}^{(k)}}{\lambda_k},$$

their values are

$$\tau_{xxxx}=\frac{9m^2a_1^2}{A_0^4\lambda_1}\left(\frac{2c_1}{a_1}A_1+\frac{B_1}{\sqrt{3}}\right)^2+\frac{9m^2a_1^2}{A_0^4\lambda_3}\left(\frac{2c_1}{a_1}A_3+\frac{B_3}{\sqrt{3}}\right)^2+\frac{9m^2a_1^2}{3A_0^4\lambda_2}B_2^2+\frac{9m^2a_1^2}{3A_0^4\lambda_4}B_4^2,$$

$$\tau_{yyyy}=\tau_{xxxx},$$

$$\tau_{zzzz}=\frac{12m^2a_1^2}{C_0^4\lambda_1}B_1^2+\frac{12m^2a_1^2}{C_0^4\lambda_3}B_3^2,$$

$$\tau_{xxyy}=\frac{9m^2a_1^2}{A_0^4\lambda_1}\left(\frac{2c_1}{a_1}A_1+\frac{B_1}{\sqrt{3}}\right)^2+\frac{9m^2a_1^2}{A_0^4\lambda_3}\left(\frac{2c_1}{a_1}A_3+\frac{B_3}{\sqrt{3}}\right)^2-\frac{9m^2a_1^2}{3A_0^4\lambda_2}B_2^2-\frac{9m^2a_1^2}{3A_0^4\lambda_4}B_4^2,$$

note that $\tau_{xxyy}=\tau_{xxzz}-2\tau_{xyxy}$,

$$\tau_{xxzz}=\frac{18m^2a_1^2}{\sqrt{3}C_0^2A_0^2\lambda_1}B_1\left(\frac{2c_1}{a_1}A_1+\frac{B_1}{\sqrt{3}}\right)+\frac{18m^2a_1^2}{\sqrt{3}C_0^2A_0^2\lambda_3}B_3\left(\frac{2c_1}{a_1}A_3+\frac{B_3}{\sqrt{3}}\right),$$

$$\tau_{yyzz}=\tau_{xxzz},$$

$$\tau_{xyxy}=\frac{9m^2a_1^2}{3A_0^4\lambda_2}B_2^2+\frac{9m^2a_1^2}{3A_0^4\lambda_4}B_4^2,$$

$$\tau_{yzyz}=\frac{36m^2c_1^2}{C_0^2A_0^2\lambda_2}A_2^2+\frac{36m^2c_1^2}{C_0^2A_0^2\lambda_4}A_4^2,$$

$$\tau_{zzzx}=\tau_{yzyz},$$

$$\tau_{xyyz}=\frac{9m^2a_1c_1}{\sqrt{3}A_0^4\lambda_2}A_2B_2+\frac{9m^2a_1c_1}{\sqrt{3}A_0^4\lambda_4}A_4B_4,$$

$$\tau_{xxzx}=-\tau_{xyyz},$$

$$\tau_{yyzx}=\tau_{xyyz}.$$

The above expressions constitute all the coefficients which are different from zero. The perturbation which we are calculating is given by considering all the possible permutations of α, β, γ and δ in such terms as $\tau_{\alpha\beta\gamma\delta}P_\alpha P_\beta P_\gamma P_\delta$. The $P_\alpha P_\beta P_\gamma P_\delta$ may be collected into six groups, each of which has the same coefficient. Thus:

$$\tau_{xxxx}\{P_xP_xP_xP_x+P_yP_yP_yP_y+P_xP_xP_yP_y+P_yP_yP_xP_x\},$$

$$\tau_{zzzz}P_zP_zP_zP_z,$$

$$\tau_{xxzz}\{P_xP_xP_zP_z+P_zP_zP_xP_x+P_yP_yP_zP_z+P_zP_zP_yP_y\},$$

$$\tau_{xyxy}\{P_xP_yP_xP_y+P_yP_xP_yP_x+P_xP_yP_yP_x+P_yP_xP_xP_y-2P_xP_xP_yP_y-2P_yP_yP_xP_x\},$$

$$\tau_{yzyz}\{P_yP_zP_yP_z+P_zP_yP_zP_y+P_yP_zP_zP_y+P_zP_yP_yP_z+P_zP_zP_xP_x+P_xP_zP_xP_z+P_xP_zP_zP_x+P_zP_xP_xP_z\},$$

$$\tau_{xyyz}\{P_xP_yP_yP_z+P_xP_yP_zP_y+P_yP_xP_yP_z+P_yP_xP_zP_y+P_yP_yP_xP_z+P_yP_yP_zP_x+P_yP_zP_xP_y+P_zP_xP_yP_y-P_xP_xP_zP_z-P_xP_zP_xP_z-P_xP_zP_zP_x-P_zP_xP_xP_z-P_zP_xP_zP_x-P_zP_zP_xP_x\}.$$

All the other $P_\alpha P_\beta P_\gamma P_\delta$'s have vanishing coefficients. Now by means of the well-known commutation rules for such matrices,

$$P^2=P_x^2+P_y^2+P_z^2,$$

P^2 commutes with all three

$$P_xP_y-P_yP_x=(\hbar/i)P_z,$$

$$P_yP_z-P_zP_y=(\hbar/i)P_x,$$

$$P_zP_x-P_xP_z=(\hbar/i)P_y,$$

the above may be reduced to much simpler matrices:

$$\tau_{xxxx}(P^4-2P^2P_z^2+P_z^4),$$

$$\tau_{zzzz}P_z^4,$$

$$\tau_{xxzz}(2P^2P_z^2-2P_z^4),$$

$$\tau_{xyxy}(5\hbar^2P_z^2-2\hbar^2P^2),$$

$$\tau_{yzyz}(4P^2P_z^2-5\hbar^2P_z^2-4P_z^4+\hbar^2P^2),$$

$$\tau_{xyyz}(8P_y^2P_zP_x+8P_xP_zP_y^2-2P^2P_xP_z-2P^2P_zP_x-4P_z^2P_x+6P_z^2P_xP_z+6P_zP_xP^2-4P_xP_z^2).$$

The eigenvalues of these matrices can now be calculated. There are many matrix representations which will satisfy the four matrix equations arising from the commutation rules. One such representation has the following nonvanishing elements:

$$(P_x)_{J,K+1}^{J,K}=i(P_y)_{J,K+1}^{J,K}=\frac{\hbar}{2}((J-K)(J+K+1))^{\frac{1}{2}},$$

$$(P_z)_{JK}{}^{JK}=\hbar K,\quad J\geqslant K.$$

This representation is chosen because in it the angular momentum P_z and the square of the total angular momentum P^2 become diagonal matrices. In this representation the W matrix has the following nonvanishing elements (in waves per cm):

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\left(\frac{1}{C_0}-\frac{1}{A_0}\right)\frac{\hbar^2}{hc_L}K^2-P_1J^2(J+1)^2+2(P_1-P_3-2P_5)K^2J(J+1)+(2P_4-P_5)J(J+1)-(P_1+P_2-2P_3-4P_5)K^4-5(P_4-P_5)K^2 \qquad (2)$$

and the off diagonal elements

$$\frac{W^{JK}_{J,K\pm1}}{hc_L}, \quad \frac{W^{JK}_{J,K\pm3}}{hc_L}$$

which are of the same order of magnitude as the last five terms in the expression above. h is Planck's constant, c_L, the velocity of light and the P's are defined by

$$P_1=\frac{\tau_{xxxx}\hbar^4}{8hc_L}, \quad P_2=\frac{\tau_{zzzz}\hbar^4}{8hc_L}, \quad P_3=\frac{\tau_{xxzz}\hbar^4}{8hc_L},$$

$$P_4=\frac{\tau_{zyzy}\hbar^4}{8hc_L}, \quad P_5=\frac{\tau_{yzyz}\hbar^4}{8hc_L}.$$

It may be shown that to a first-order approximation the off diagonal elements can be neglected. To this approximation, therefore, the W matrix is diagonal with elements given by expression (2).

Thus far the P's have been given in terms of the normalized first minors of the determinants formed by the coefficients of the kinetic and potential energies. One may show, however, that:

$$\frac{A_1^2}{\lambda_1}+\frac{A_3^2}{\lambda_3}=\frac{b}{ab-c^2}, \qquad \frac{A_2^2}{\lambda_2}+\frac{A_4^2}{\lambda_4}=\frac{\beta}{\alpha\beta-\gamma^2},$$

$$\frac{B_1^2}{\lambda_1}+\frac{B_3^2}{\lambda_3}=\frac{a}{ab-c^2}, \qquad \frac{B_2^2}{\lambda_2}+\frac{B_4^2}{\lambda_4}=\frac{\alpha}{\alpha\beta-\gamma^2},$$

$$\frac{A_1B_1}{\lambda_1}+\frac{A_3B_3}{\lambda_3}=-\frac{c}{ab-c^2},$$

$$\frac{A_2B_2}{\lambda_2}+\frac{A_4B_4}{\lambda_4}=-\frac{\gamma}{\alpha\beta-\gamma^2},$$

so that the P's have the more easily calculable form:

$$P_1=G\left\{4c_1^2\frac{b}{ab-c^2}-\frac{4a_1c_1}{\sqrt{3}}\frac{c}{ab-c^2}+\frac{a_1^2}{3}\frac{a}{ab-c^2}+\frac{a_1^2}{3}\frac{\alpha}{\alpha\beta-\gamma^2}\right\},$$

$$P_2=\frac{1}{4}\left(\frac{2A_0}{C_0}\right)^4 G\left\{\frac{a_1^2}{3}\frac{a}{ab-c^2}\right\},$$

$$P_3=\frac{1}{2}\left(\frac{2A_0}{C_0}\right)^2 G\left\{-\frac{2a_1c_1}{\sqrt{3}}\frac{c}{ab-c^2}+\frac{a_1^2}{3}\frac{a}{ab-c^2}\right\},$$

$$P_4=G\left\{\frac{a_1^2}{3}\frac{\alpha}{\alpha\beta-\gamma^2}\right\},$$

$$P_5=G\left\{c_1^2\frac{\beta}{\alpha\beta-\gamma^2}\right\},$$

where $G\equiv 9m^2\hbar^4/8c_LhA_0^4$.

Expression (2) is perfectly general insofar as it will hold for any ammonia-like molecule as for example ND_3, PH_3, PD_3, AsH_3, AsD_3, etc. The numerical calculation involves the dimensions of the particular molecule and its force constants. These are often obtainable from the vibrational spectrum, and the fine structure of these vibrational bands. The dimensions of both NH_3, and ND_3 are well known from the work of Migeotte and Barker,[7] Wright and Randall,[3] Dennison and Uhlenbeck.[8] The force constants for these two molecules have also been evaluated by Migeotte and Barker but in coordinates which are different from ours. The transformation to our coordinates is, however, straight forward.

The various constants for NH_3 are:

$$\begin{aligned}
a&=5.46\times10^5 \text{ dynes/cm},\\
b&=5.04\times10^5 \text{ dynes/cm},\\
c&=4.23\times10^5 \text{ dynes/cm},\\
A_0&=2.782\times10^{-40} \text{ g cm}^2,\\
a_1&=0.950\times10^{-8} \text{ cm},\\
\alpha&=10.16\times10^5 \text{ dynes/cm},\\
\beta&=3.54\times10^5 \text{ dynes/cm},\\
\gamma&=3.67\times10^5 \text{ dynes/cm},\\
C_0&=4.497\times10^{-40} \text{ g cm}^2,\\
c_1&=0.296\times10^{-8} \text{ cm}.
\end{aligned}$$

The constants for ND_3 are identical with those for NH_3 except that $A_0=5.397\times10^{-40}$, $C_0=8.985\times10^{-40}$ and $c_1=0.275\times10^{-8}$. These values give for δW, the change in the energy due to the

[7] M. V. Migeotte and E. F. Barker, Phys. Rev. **50**, 418 (1936).

[8] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).

rotational distortion:

$$\frac{\delta W}{hc_L} = -0.000625J^2(J+1)^2 + 0.000950K^2J(J+1) + 0.000799J(J+1) - 0.000630K^4 - 0.00189K^2 \quad (3)$$

and for ND_3,

$$\frac{\delta W}{hc_L} = -0.000176J^2(J+1)^2 + 0.000261K^2J(J+1) + 0.000226J(J+1) - 0.000163K^4 - 0.000540K^2. \quad (4)$$

The pure rotation frequencies are then obtained by means of the selection rules. For all ammonia-like molecules these are: $\Delta K = 0$ and $\Delta J = \pm 1$. The frequencies are then given by:

$$\nu_J{}^{J-1} = \frac{\hbar^2}{A_0 hc_L} J + 0.00160J - 0.00250J^3 + 0.00190K^2J \quad (5)$$

for NH_3 and

$$\nu_J{}^{J-1} = \frac{\hbar^2}{A_0 hc_L} J + 0.000452J - 0.000704J^3 + 0.000522K^2J \quad (6)$$

for ND_3.

It is evident from the last term in (5) and (6) that the far infra-red lines of these molecules have a fine structure. For NH_3 the spacing is given by $0.00190J(2K-1)$ where K is taken for the larger component. This spacing is much too small to be observed for lines with J values less than 15. However, their presence will affect the position of the peak of any experimentally observed line. Such a peak will be roughly at the center of gravity of the fine structure components. Therefore, in order to compare the theoretical values with those observed, one must consider the intensity pattern of a given line and determine its center of gravity.

The rotation lines of NH_3 consist of close doublets which are caused by the existence of a double minimum for the N atom. This complication must be considered in calculating the intensity patterns.

The double minimum problem has been treated by several authors.[8, 9] It is shown that in the pure-rotation spectrum there are two vibrational energy levels for each value of J, one of these belongs to the symmetric solutions the other to the antisymmetric. The first are commonly designated by α and the latter by β. The selection rules are such that only transitions from α to β or β to α are allowed. The doublet member on the long wave-length side corresponds to the β to α transition while the other arises from the α to β transition. The doublet separation for the case of pure rotation will be just twice the separation of the α and β levels in the zeroth vibrational state and is independent of J.

The intensity formula has been given explicitly by Dennison and Hardy[9] and may be immediately adapted to our case.

$$I = A\nu_{K'}{}^{K}[x]\frac{J^2-K^2}{J}e^{-\sigma(J^2+J)-\sigma\beta K^2}(1-e^{-h\nu/KT}).$$

Since only the shape of the line, rather than its absolute intensity is of interest, we may reject all multiplicative constants, thus:

$$I \cong \nu_{K'}{}^{K}[x](J^2-K^2)e^{-\sigma\beta K^2}(1-e^{-h\nu/KT}),$$

$\sigma \equiv \hbar^2/2A_0KT$ and $\beta = (A_0/C_0 - 1)$. $[x]$ is the weight factor which has the following values: if the component under consideration is due to a transition for which $K=0$, J even, and the final state α, then $[x]=0$; if the final state is β, then $[x]=2$. If J is odd, then the converse is true. For $K \neq 0$ and not a multiple of 3, then regardless of whether the final state is an α or a β state, $[x]=1$. If K is a multiple of 3, then $[x]=2$ for both α and β final states.

As an example, the results of the calculation will be given in detail for $J=7$. In Table I the $(-)$ sign designates the long wave-length component of the doublet. The exact position of the maximum when such lines are unresolved is, of course, difficult to predict. It was assumed that it is given by the center of gravity of the components. We have, therefore, $\Delta_+ = 0.187$ and

[9] Dennison and Hardy, Phys. Rev. **39**, 938 (1932). Dennison, Rev. Mod. Phys. **3**, 208 (1931). F. Hund, Zeits. f. Physik **43**, 805 (1927).

$\Delta_-=0.144$ where the Δ's are measured from the component for which $K=0$, and hence from the position where the maximum would be if there were no JK^2 term. The experimental curve for this line as observed by Wright and Randall together with the theoretically calculated components are shown in Fig. 3. For $J=6$, $\Delta_+=0.074$ and $\Delta_-=0.103$ and for $J=5$, the third line observed by Wright and Randall, $\Delta_+=0.064$ and $\Delta_-=0.042$.

The exact frequencies may now be calculated and compared with the observed frequencies. Since the doublet separation is independent of J, we take the average value, i.e., 1.32 cm^{-1}. The single adjustable parameter, the A_0 moment of inertia, may be adjusted to fit any one of the frequencies and the rest then calculated. With $\hbar^2/A_0hc_L=19.890$ we have the results shown in Table II.

This comparison together with Fig. 3 which shows that the observed curve fits the calculated components well, indicates that the theory is adequate for the explanation of this spectrum.

Barnes[4] has mapped the far infra-red spectrum of NH_3 for J values up to 12, but unfortunately the resolving power is not as good as that obtained by Wright and Randall and the results, therefore, not quite so accurate. The doublet separation is not in evidence. We have calculated a few of these lines to see how well our calculations fit the observed lines. In doing so, the intensity patterns of the two members of the doublet were superimposed, and the center of gravity of the resultant pattern taken as the position of the peak of the line. (Table III.)

The pure rotation spectrum of ND_3 is completely determined by the data already known from NH_3. The dimensions and the force constants are the same for both molecules and the

TABLE I.

K	0.0019 JK^2	(J^2-K^2) [x] (−)	(J^2-K^2) [x] (+)	B.F.	I_-	I_+
0	0.000	98.0	0.0	1.000	98.0	0.0
1	0.013	48.0	48.0	1.019	48.9	48.9
2	0.053	45.0	45.0	1.076	48.4	48.4
3	0.122	80.0	80.0	1.180	94.4	94.4
4	0.214	33.0	33.0	1.343	44.4	44.4
5	0.324	24.0	24.0	1.587	38.0	38.0
6	0.480	26.0	26.0	1.947	50.6	50.6

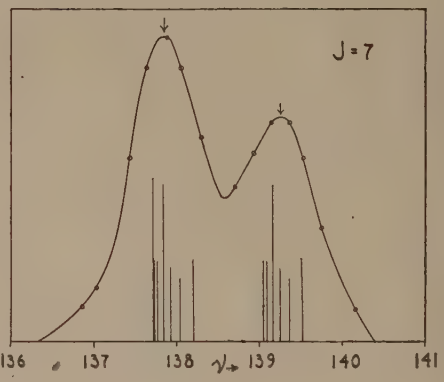

FIG. 3.

moments of inertia may be calculated from the mass of deuterium and the dimensions of the molecule. The frequencies are given by:

$$\nu_J{}^{J-1}=10.260J+0.000452J -0.000704J^3+0.000522K^2J.$$

Barnes has mapped the ND_3 lines with the same arrangement he used for NH_3 and presumably with the same accuracy. In Table IV some of the calculated lines are compared with the experimental values.

It is perhaps of interest to note that the usual procedure of fitting a cubic expression such as $AJ-BJ^3$ to the observed frequencies gives very nearly the correct values. From theoretical considerations, however, a JK^2 term should be included. It turns out that the center of gravity of the components is roughly given by one-third the coefficient of the JK^2 term multiplied by J^3 so that the theoretical values will approximately follow a simple cubic expression. The divergence from this simple formula will, of course, become evident when J values are high enough to spread out the fine structure components.

We have also calculated the far infra-red spectrum of PH_3, four lines of which have been mapped by Wright and Randall under high resolving power. These calculations suffer, however, from the fact that the infra-red frequencies of this molecule are not well known so that neither the dimensions nor the force constants can be determined with any degree of accuracy. We have taken the values as given by Howard.[10]

[10] J. B. Howard, J. Chem. Phys. **3**, 207 (1935).

He calculates the force constants on the assumption that the molecule is of the valence type. Under this assumption only two fundamental frequencies are needed to determine the two force constants, which he calls K and H. K is the constant which gives the resistance to the stretching of the P−H bond and H is the constant which gives the resistance to the deformation of the H−P−H angle. The values are: $K=3.09\times10^5$ and $H=0.34\times10^5$ dynes/cm. The dimensions of this molecule may be estimated and give for the moment of inertia, A_0, 6.221×10^{-40}, and for C_0, 7.73×10^{-40}. The dimension, a_1, is 1.24×10^{-8} and c_1 is 0.657×10^{-8}. With these values one may deduce the general force constants, a, b, c, and α, β, γ, from the constants K and H. They turn out to be:

$$a=3.63\times10^5 \text{ dynes/cm},$$
$$b=7.39\times10^5 \text{ dynes/cm},$$
$$c=3.26\times10^5 \text{ dynes/cm},$$
$$\alpha=3.97\times10^5 \text{ dynes/cm},$$
$$\beta=1.61\times10^5 \text{ dynes/cm},$$
$$\gamma=1.53\times10^5 \text{ dynes/cm}.$$

The pure rotation energy of PH_3 is then given by:

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\left(\frac{1}{C_0}-\frac{1}{A_0}\right)\frac{\hbar^2K^2}{hc_L}$$
$$-0.000123J^2(J+1)^2+0.000155K^2J(J+1)$$
$$+0.000104J(J+1)-0.000105K^4-0.000208K^2.$$

Since the selection rules are identically the same as those for NH_3, the change in the energy due to the centrifugal distortion is, in waves per cm:

$$\Delta\nu_J{}^{J-1}=0.000208J+0.000310JK^2-0.000492J^3.$$

It must be pointed out that neither the fundamental frequencies nor the dimensions are really well established for PH_3. The above formulae are therefore somewhat inaccurate. They may, nevertheless, serve well for locating other pure rotation lines of phosphine. We have calculated one of the lines which have been observed by Wright and Randall ($J=13$) and obtained 114.66 as against the observed value, 114.84; a fair check considering the inaccuracy of the data used.

TABLE II.

J FINAL	CALC.	OBS.	DEV.
5	98.52	98.53	+0.01
5	99.86	99.83	−0.03
6	118.25	118.22	−0.03
6	119.54	119.58	+0.04
7	137.86	137.88	+0.02
7	139.23	139.21	−0.02

THE ZYX_3 MOLECULE

There are a number of molecules of the ZYX_3 type whose infra-red spectrum has been the subject of considerable study. Since all such molecules have a permanent electric dipole moment, they have a far infra-red spectrum. We propose to extend our calculations to such molecules and in particular evaluate numerically the spectrum of the methyl halides.

The geometrical configuration of the ZYX_3 molecule is indicated in Fig. 4. The YX_3 group of atoms in this molecule has the same geometrical configuration as the YX_3 molecule discussed in the previous section. The Z atom is located along the axis of the YX_3 pyramid.

In a manner similar to that used for the YX_3 molecule, we may set up the moments of inertia, A, B, C, and the products of inertia, D, E, and F, in terms of the equilibrium positions of the atoms and of their displacements from equilibrium. The internal coordinates are then introduced by means of the conditions for the conservation of linear and angular momenta. For the conservation of linear momentum:

$$M_2\dot{z}_5+M_1\dot{z}_4+3m\dot{z}_{123}=0,$$
$$M_2\dot{x}_5+M_1\dot{x}_4+3m\dot{x}_{123}=0,$$
$$M_2\dot{y}_5+M_1\dot{y}_4+3m\dot{y}_{123}=0,$$

and for the conservation of the angular momentum:

$$M_2a_0\dot{x}_5+M_1b_0\dot{x}_4+\tfrac{1}{2}C_0\dot{\theta}=0, \quad a_0\equiv c_3+c_1,$$
$$M_2a_0\dot{y}_5+M_1b_0\dot{y}_4+\tfrac{1}{2}C_0\dot{\theta}=0, \quad b_0=c_1-c_2.$$

TABLE III.

J FINAL	CALC.	OBS.	DEV.
8	158.11	158.33	−0.22
9	177.58	177.69	−0.11
10	197.06	196.93	+0.13
11	216.32	216.61	−0.29

TABLE IV.

J FINAL	CALC.	OBS.	DEV.
10	102.08	102.32	−0.24
15	152.36	152.02	+0.34
16	162.13	162.12	+0.01
17	172.01	172.10	−0.09
18	181.88	181.99	−0.11
19	191.79	192.80	−1.01
20	201.59	202.10	−0.51

In the above equations M_2, M_1 and m are the masses of the Z, Y and the X atoms, respectively; c_1 is the equilibrium distance of the center of gravity of the three X atoms from the center of gravity of the molecule; c_2 and c_3 are the equilibrium distances of Y and Z atoms, respectively, from the center of gravity of the molecule; x_5, y_5, z_5 are the displacements of the Z atom from equilibrium, x_4, y_4, z_4 that of the Y atom and x_{123}, y_{123}, z_{123} are the displacements of any one of the X atoms from its position of equilibrium. θ is the angle between the perpendicular to the plane of the X atoms and the line drawn through the center of gravity of the X atoms, the Y and the Z atoms. (See Fig. 5.) C_0 is, as in the case of NH_3, the moment of inertia about the axis of symmetry when the molecule is considered rigid.

The coordinates which we introduce give the displacement of Z with respect to Y and Y with respect to the center of gravity of the X atoms. Together with coordinates ξ, η and ζ, already described, we have the nine coordinates necessary to describe the internal motions of the molecule. The new coordinates are determined by:

$$p=x_5-x_4, \quad q=y_5-y_4, \quad r=z_5-z_4,$$

$$x=x_4-x_{123}, \quad y=y_4-y_{123}, \quad z=z_4-z_{123},$$

thus

$$x_{123}=-\frac{M_2}{\Sigma}p-\frac{M_1+M_2}{\Sigma}x,$$

$$x_4=-\frac{M_2}{\Sigma}p+\frac{3m}{\Sigma}x,$$

$$x_5=+\frac{\Sigma'}{\Sigma}p+\frac{3m}{\Sigma}x,$$

with similar expressions for Y and Z.

$$\theta=-\frac{2}{C_0}\{M_2c_3p+3mc_1x\},$$

here $\Sigma=M_2+M_1+3m$ and $\Sigma'=M_1+3m$.

The moments and products of inertia expressed in these coordinates assume the following simple form:

$$A=A_0+6mc_1z+2M_2c_3r+3ma_1(\zeta+\xi),$$

$$B=B_0+6mc_1z+2M_2c_3r+3ma_1(\zeta-\xi),$$

$$C=C_0+6ma_1\zeta,$$

$$D=3ma_1\eta,$$

$$E=6mc_1y+2M_2c_3q,$$

$$F=6mc_1x+2M_2c_3p.$$

The coordinates p and x or q and y suffer the disadvantage of depending on the masses rather than on the geometric properties of the molecule. We therefore introduce the coordinates X_1, X_2 and Y_1, Y_2 as illustrated in Fig. 5.

$$X_1=p-\frac{a_0-b_0}{b_0}x, \quad Y_1=q-\frac{a_0-b_0}{b_0}y,$$

$$X_2=x-b_0\theta, \quad Y_2=y-b_0\theta.$$

When these relations are solved for p, x, q and y and the values substituted in E and F, they become:

$$E=\frac{C_0}{2A_0}\left\{2M_2c_3Y_1+\frac{2}{b_0}(A_0-\tfrac{1}{2}C_0)Y_2\right\},$$

$$F=\frac{C_0}{2A_0}\left\{2M_2c_3X_1+\frac{2}{b_0}(A_0-\tfrac{1}{2}C_0)X_2\right\}.$$

The normal coordinates are introduced by means

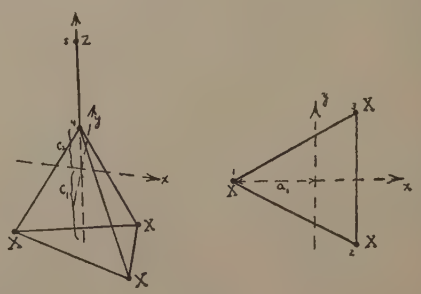

FIG. 4.

of the usual determinant of the kinetic and potential energies. Just as in the case of NH_3 the Hamiltonian for the ZYX_3 molecule splits up into two parts, one giving the motions belonging to the parallel bands and the other those giving the perpendicular bands.

The kinetic energy expressions for the parallel vibrations are:

$$2T_{\parallel}=M_2\dot{z}_5^2+M_1\dot{z}_4^2+3m\dot{z}_{123}^2+3m\dot{\zeta}^2,$$

and for the perpendicular:

$$2T_{\perp}=M_2\dot{x}_5^2+M_1\dot{x}_4^2+3m\dot{x}_{123}^2+\frac{C_0}{2}\dot{\theta}^2+3m\dot{\xi}^2.$$

Since the expressions for the y direction are always identical with those given above for the x direction, we shall consistently omit them where no ambiguity exists.

Together with the expressions for the potential energies these may be written in terms of the coordinates described above.

$$2T_{\parallel}=a_{11}\dot{r}^2+a_{33}\dot{z}^2+2a_{13}\dot{r}\dot{z}+3m\dot{\zeta}^2,$$

$$2V_{\parallel}=ar^2+bz^2+c\zeta^2+2drz+2er\zeta+2fz\zeta,$$

and for the perpendiculars:

$$2T_{\perp}=a_{22}\dot{X}_1^2+a_{44}\dot{X}_2^2+2a_{24}\dot{X}_1\dot{X}_2+3m\dot{\xi}^2,$$

$$2V_{\perp}=\alpha X_1^2+\beta X_2^2+\gamma\xi^2+2\delta X_1X_2+2\epsilon X_1\xi+2\varphi X_2\xi.$$

The constants a, b, c, d, e, f, α, β, γ, δ, ϵ and φ are the usual force constants of the molecule. The evaluation of these constants is the subject of another paper.[11] The other constants are as follows:

$$a_{11}=\frac{M_2\Sigma'}{\Sigma},\qquad a_{22}=\frac{3mM_1M_2b_0^2+M_2(C_0/2)\Sigma'}{A_0\Sigma},$$

$$a_{33}=\frac{3m(M_1+M_2)}{\Sigma},\qquad a_{44}=\frac{(A_0-C_0/2)C_0/2}{A_0b_0^2},$$

$$a_{13}=\frac{3mM_2}{\Sigma},\qquad a_{24}=\frac{M_2(3ma_0+M_1a_0-M_1b_0)C_0/2}{A_0b_0\Sigma}.$$

Once the kinetic and potential energies are known, the transformation to the normal co-

[11] Succeeding paper by the authors.

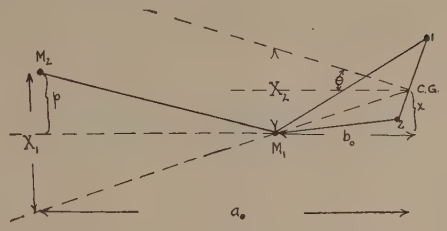

FIG. 5.

ordinates is given by:

$$z=A_1Q_1+A_3Q_3+A_5Q_5,$$

$$X_2=A_2Q_2+A_4Q_4+A_6Q_6,$$

$$\zeta=B_1Q_1+B_3Q_3+B_5Q_5,$$

$$\xi=B_2Q_2+B_4Q_4+B_6Q_6,$$

$$r=D_1Q_1+D_3Q_3+D_5Q_5,$$

$$X_1=D_2Q_2+D_4Q_4+D_6Q_6.$$

The coefficients for Y_1, Y_2 and η are identical with those for X_1, X_2 and ξ.

The coefficients $A_1\cdots D_6$ are the normalized first minors of the following determinants.

For the parallel frequencies,

$$\begin{vmatrix} a_{11}\lambda-a & a_{13}\lambda-d & -e \\ a_{13}\lambda-d & a_{33}\lambda-b & -f \\ -e & -f & 3m\lambda-c \end{vmatrix}=0,$$

and for the perpendiculars:

$$\begin{vmatrix} a_{22}\lambda-\alpha & a_{24}\lambda-\delta & -\epsilon \\ a_{24}\lambda-\delta & a_{44}\lambda-\beta & -\varphi \\ -\epsilon & -\varphi & 3m\lambda-\gamma \end{vmatrix}=0.$$

The first minors of these determinants are:

$$U_i=(a_{33}e-a_{13}f)\lambda_i+df-be, \qquad i=1,3,5,$$

$$V_i=-\{(a_{13}e-a_{11}f)\lambda_i+af-de\},$$

$$W_i=(a_{11}a_{33}-a_{13}^2)\lambda_i^2-(a_{11}b+a_{33}a-2a_{13}d)\lambda_i+ab-d^2,$$

$$U_j=(a_{44}\epsilon-a_{24}\varphi)\lambda_j+\delta\varphi-\beta\epsilon, \qquad j=2,4,6,$$

$$V_j=-\{(a_{24}\epsilon-a_{22}\varphi)\lambda_j+\alpha\varphi-\delta\epsilon\},$$

$$W_j=(a_{22}a_{44}-a_{24}^2)\lambda_j^2-(a_{22}\beta+a_{44}\alpha-2a_{24}\delta)\lambda_j+\alpha\beta-\delta^2.$$

The normalized first minors are then:

$$D_i=\frac{U_i}{(a_{11}U_i^2+a_{33}V_i^2+2a_{13}U_iV_i+3mW_i^2)^{\frac{1}{2}}},$$

$$D_j=\frac{U_j}{(a_{22}U_j^2+a_{44}V_j^2+2a_{24}U_jV_j+3mW_j^2)^{\frac{1}{2}}},$$

$$A_i=\frac{V_i}{U_i}D_i,\quad B_i=\frac{W_i}{U_i}D_i,\quad A_j=\frac{V_j}{U_j}D_j,\quad B_j=\frac{W_j}{U_j}D_j.$$

Comparison with the NH_3 case shows immediately that the matrices for this type of molecule fall into the same groupings. The coefficients are, of course, different and more complicated for numerical evaluation. For the same reasons as have been given for the YX_3 molecule, the energy matrix, including the rotational distortion is diagonal to the order of approximation used here. The rotational energy levels are then given by an expression which formally is identical with (2). The P's, however, are now given by:

$$P_1=G\Big\{4c_1^2\Big(\frac{A_1^2}{\lambda_1}+\frac{A_3^2}{\lambda_3}+\frac{A_5^2}{\lambda_5}\Big)+4a_1c_1\Big(\frac{A_1B_1}{\lambda_1}+\frac{A_3B_3}{\lambda_3}+\frac{A_5B_5}{\lambda_5}\Big)+a_1^2\Big(\frac{B_1^2}{\lambda_1}+\frac{B_3^2}{\lambda_3}+\frac{B_5^2}{\lambda_5}\Big)+\frac{4M_2^2c_3^2}{9m^2}\Big(\frac{D_1^2}{\lambda_1}+\frac{D_3^2}{\lambda_3}+\frac{D_5^2}{\lambda_5}\Big)+\frac{24mc_1M_2c_3}{9m^2}\Big(\frac{A_1D_1}{\lambda_1}+\frac{A_3D_3}{\lambda_3}+\frac{A_5D_5}{\lambda_5}\Big)+\frac{4M_2c_3a_1}{3m}\Big(\frac{B_1D_1}{\lambda_1}+\frac{B_3D_3}{\lambda_3}+\frac{B_5D_5}{\lambda_5}\Big)+a_1^2\Big(\frac{B_2^2}{\lambda_2}+\frac{B_4^2}{\lambda_4}+\frac{B_6^2}{\lambda_6}\Big)\Big\},$$

$$P_2=\frac{1}{4}\Big(\frac{2A_0}{C_0}\Big)^4Ga_1^2\Big(\frac{B_1^2}{\lambda_1}+\frac{B_3^2}{\lambda_3}+\frac{B_5^2}{\lambda_5}\Big),$$

$$P_3=\frac{1}{2}\Big(\frac{2A_0}{C_0}\Big)^2G\Big\{2a_1c_1\Big(\frac{A_1B_1}{\lambda_1}+\frac{A_3B_3}{\lambda_3}+\frac{A_5B_5}{\lambda_5}\Big)+a_1^2\Big(\frac{B_1^2}{\lambda_1}+\frac{B_3^2}{\lambda_3}+\frac{B_5^2}{\lambda_5}\Big)+\frac{2M_2a_1c_3}{3m}\Big(\frac{B_1D_1}{\lambda_1}+\frac{B_3D_3}{\lambda_3}+\frac{B_5D_5}{\lambda_5}\Big)\Big\},$$

$$P_4=Ga_1^2\Big(\frac{B_2^2}{\lambda_2}+\frac{B_4^2}{\lambda_4}+\frac{B_6^2}{\lambda_6}\Big),$$

$$P_5=G\Big\{\frac{M_2^2c_3^2}{9m^2}\Big(\frac{D_2^2}{\lambda_2}+\frac{D_4^2}{\lambda_4}+\frac{D_6^2}{\lambda_6}\Big)+\frac{(A_0-C_0/2)^2}{9m^2b_0^2}\Big(\frac{A_2^2}{\lambda_2}+\frac{A_4^2}{\lambda_4}+\frac{A_6^2}{\lambda_6}\Big)+\frac{2M_2c_3}{9m^2b_0}\Big(A_0-\frac{C_0}{2}\Big)\Big(\frac{A_2D_2}{\lambda_2}+\frac{A_4D_4}{\lambda_4}+\frac{A_6D_6}{\lambda_6}\Big)\Big\}.$$

The numerical calculation of the P's turns out to be rather involved since it seems to be impossible to reduce them to expressions as simple as those for ammonia-like molecules. By using the dimensions and force constants discussed in the succeeding paper we obtained the values given in Table V.

The change in the rotational energy levels in these methyl halides due to the centrifugal force stretching may then be immediately written as

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\Big(\frac{1}{C_0}-\frac{1}{A_0}\Big)\frac{\hbar^2}{hc_L}K^2-4.34\times10^{-7}J^2(J+1)^2+1.45\times10^{-5}K^2J(J+1)-3.23\times10^{-6}J(J+1)-7.02\times10^{-4}K^4+1.67\times10^{-5}K^2$$

for FCH_3,

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\Big(\frac{1}{C_0}-\frac{1}{A_0}\Big)\frac{\hbar^2}{hc_L}K^2-1.14\times10^{-7}J^2(J+1)^2+0.976\times10^{-5}K^2J(J+1)-1.71\times10^{-6}J(J+1)-7.52\times10^{-4}K^4+0.861\times10^{-5}K^2$$

TABLE V.

	FCH$_3$	ClCH$_3$	BrCH$_3$	ICH$_3$
10^7 P_1	4.34	1.14	0.30	0.38
10^4 P_2	6.88	7.43	8.46	10.83
10^6 P_3	−13.70	−8.23	−4.71	−6.18
10^8 P_4	10.75	1.04	0.22	0.096
10^7 P_5	34.46	17.32	6.94	5.30

for ClCH$_3$,

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\left(\frac{1}{C_0}-\frac{1}{A_0}\right)\frac{\hbar^2}{hc_L}K^2$$
$$-0.30\times10^{-7}J^2(J+1)^2$$
$$+0.670\times10^{-5}K^2J(J+1)$$
$$-0.690\times10^{-6}J(J+1)$$
$$-8.52\times10^{-4}K^4+0.346\times10^{-5}K^2$$

for BrCH$_3$, and

$$\frac{W_{JK}{}^{JK}}{hc_L}=\frac{\hbar^2}{2A_0hc_L}J(J+1)+\left(\frac{1}{C_0}-\frac{1}{A_0}\right)\frac{\hbar^2}{hc_L}K^2$$
$$-0.38\times10^{-7}J^2(J+1)^2$$
$$+0.832\times10^{-5}K^2J(J+1)$$
$$-0.528\times10^{-6}J(J+1)$$
$$-10.93\times10^{-4}K^4+0.264\times10^{-5}K^2$$

for ICH$_3$.

Applying the selection rules which are $\Delta J=1$, $\Delta K=0$ we obtain the following rotational frequencies.

$$\nu_J{}^{J-1}=\frac{\hbar^2}{A_0hc_L}J-6.46\times10^{-6}J$$
$$-1.736\times10^{-6}J^3+2.90\times10^{-5}K^2J$$

for FCH$_3$,

$$\nu_J{}^{J-1}=\frac{\hbar^2}{A_0hc_L}J-3.42\times10^{-6}J$$
$$-4.56\times10^{-7}J^3+1.952\times10^{-5}K^2J$$

for ClCH$_3$,

$$\nu_J{}^{J-1}=\frac{\hbar^2}{A_0hc_L}J-1.380\times10^{-6}J$$
$$-1.20\times10^{-7}J^3+1.340\times10^{-5}K^2J$$

for BrCH$_3$, and

$$\nu_J{}^{J-1}=\frac{\hbar^2}{A_0hc_L}J-1.056\times10^{-6}J$$
$$-1.52\times10^{-7}J^3+1.664\times10^{-5}K^2J$$

for ICH$_3$.

Unfortunately the pure rotation spectra of these molecules have not as yet been mapped so that comparison with experimental values must be left to the future.

Printed in U. S. A.

The Potential Functions of the Methyl Halides

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(Received May 1, 1939)

The problem of the potential functions of the methyl halides is re-examined in an attempt to find a function which is both adequate and simple. A valence form of potential was tried which contained four constants: k_1, the C−H elongation; c, the C−X elongation; k_2, the deformation of the H−C−H angle; and k_3, the deformation of the X−C−H angle. It was found that this simple valence potential must be modified by the inclusion of a cross product term between the X−C distance and the X−C−H angle, thus introducing a fifth constant, k_4.

The constants k_1 and k_2 were determined from the methane frequencies ($k_1=4.88\times10^5$ and $k_2=0.443\times10^5$) and were taken to be the same for all the methyl halides. By adjusting the three remaining constants it was possible to predict eight quantities, the six fundamental frequencies and two of the fine structure spacings. The agreement with the observed values was satisfactory, the average deviation being less than 1 percent.

THE infra-red spectra of the methyl halides were investigated by Bennett and Meyer[1] in 1928 and since then a number of attempts have been made to obtain a potential energy function which will adequately describe these molecules. Sutherland and Dennison[2] have treated the parallel motions of FCH_3, $ClCH_3$, $BrCH_3$ and ICH_3 while Voge and Rosenthal[3] have considered the vibrations of the $ClCH_3$ molecule. In both cases the authors have chosen potential functions with as many or nearly as many arbitrary constants as could be determined by means of the available experimental data. In this paper the normal vibrations of these molecules are re-examined in an attempt to find a potential function which is physically plausible, simple, and yet adequate for the explanation of the observed bands and their fine structure spacings.

The geometrical configuration of these molecules has already been described in the preceding paper. In assuming a potential function we were guided by the following considerations: It is well known from the work of Rosenthal on methane,[4] Howard on ammonia,[5] and Cross and Van Vleck on water[6] that these molecules, possessing a heavy atom together with several hydrogen atoms, have potential fields closely approximating the so-called valence type. That is, the potential energy depends only on the distance of each hydrogen atom from the heavy atom and upon the angles between the bond directions. Thus in the case of methane the potential energy may be given by two constants, k_1, which determines the resistance to the stretching of the carbon-hydrogen bond and k_2, which gives the resistance to the deformation of the H−C−H angle. It is also well known that molecules containing two or more heavy atoms, as for example CCl_4, cannot be treated by means of a valence type potential. We have therefore made two assumptions about the force field of the methyl halides. First, that the methyl group is bound by the valence type forces, the same for all the members of the series, and in fact, identical with those occurring in methane. Secondly, that the forces which bind the halogen atom to the methyl group are of a more general type.

In accordance with the above assumptions each methyl halide molecule requires five force constants for its potential energy function. Two of these, k_1 and k_2, have already been mentioned. The third constant describes the change in the potential energy when the halogen-carbon bond is stretched, while the fourth constant measures the energy change for a deformation of the X−C−H angles. The fifth gives the interaction term between the last two, that is, it indicates the change in the resistance to the deformation of the X−C−H angle when the X−C bond is stretched, and vice versa. The last three constants will be designated by c, k_3 and k_4, respectively. Since k_1

[1] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).
[2] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **148**, 250 (1935).
[3] H. H. Voge and J. E. Rosenthal, J. Chem. Phys. **4**, 137 (1936).
[4] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).
[5] J. B. Howard, J. Chem. Phys. **3**, 207 (1935).
[6] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

and k_2 are adjusted to satisfy the methane frequencies, only the last three constants have to be evaluated from the normal frequencies of the methyl halides.

Each methyl halide has six fundamental bands. Three of these suffice for the adjustment of the three remaining constants and hence there are three more to act as checks on our assumptions. Aside from this, when the potential energy constants are known, one may calculate the fine structure of the perpendicular bands. This fine structure spacing is very sensitive to these constants and therefore gives us another good test for the assumed potential functions.

The assumed potential energy is of the form:

$$2V=k_1\sum_i(\delta r_i)^2+k_2\sum_i(\delta\alpha_i)^2$$
$$+k_3r_0^2\sum_i(\delta\beta_i)^2+c(\delta x_0)^2+2k_4r_0(\delta x_0)\sum_i(\delta\beta_i),$$

where i takes on the values 1, 2, 3, corresponding to the three hydrogen atoms in the methyl group. The coordinates are illustrated in Fig. 1. x_0 is the X−C distance at equilibrium, r_0 the H−C distance, β_i the X−C−H angle and α_i the H−C−H angle. δr_i corresponds then to the stretching of the C−H bond, $\delta\alpha_i$ the deformation in the H−C−H angle, δx_0 the change in the distance from carbon to the halogen atom and $\delta\beta_i$ the change in the X−C−H angle.

In a paper by Rosenthal and Voge[7] the most general potential functions for the parallel and perpendicular frequencies of the ZYX_3 molecule, the kinetic energy and the resulting cubic equations, which determine the frequencies, are explicitly written out. We shall therefore obtain the relationship between their general force constants and ours and thus arrive at the cubic equations in terms of our potential constants.

The cubic equation for the parallel frequencies as given in their paper is

$$\lambda_{\parallel}^3+R_1\lambda_{\parallel}^2+R_2\lambda_{\parallel}+R_3=0, \qquad (1)$$

where the R's are functions of the force constants G_{ij} of the potential energy function

$$2V_{\parallel}=G_{11}s_1^2+G_{22}s_2^2+G_{33}s_3^2$$
$$+2G_{12}s_1s_2+2G_{13}s_1s_3+2G_{23}s_2s_3.$$

[7] J. E. Rosenthal and H. H. Voge, J. Chem. Phys. **4**, 134 (1936).

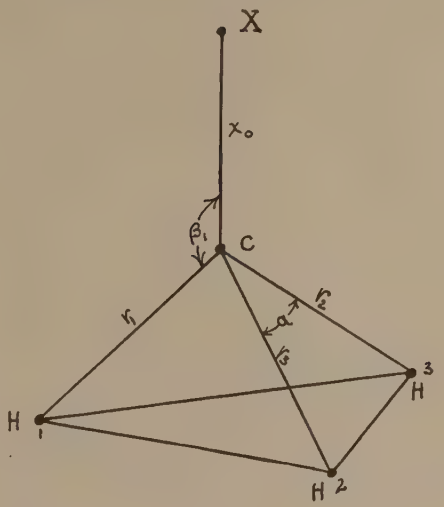

FIG. 1.

It is convenient to give the λ's in such units that $\lambda_i=4\pi^2\nu_i^2mc_L^2$ where m is the mass of an hydrogen atom. The cubic for the perpendicular frequencies is:

$$\lambda_{\perp}^3+P_1\lambda_{\perp}^2+P_2\lambda_{\perp}+P_3=0 \qquad (2)$$

and again the P's are functions of the G_{kl}'s of the potential energy expression

$$2V_{\perp}=G_{44}s_4^2+G_{55}s_5^2+G_{66}s_6^2$$
$$+2G_{45}s_4s_5+2G_{56}s_5s_6+2G_{46}s_4s_6.$$

These functions are given explicitly in the papers mentioned.

The coordinate system that is used by Rosenthal and Voge is illustrated in Fig. 2. r_i is the distance of any hydrogen atom from the carbon atom, r_4 is the X−C distance, q_{ij} the H−H distance, q_{i4} the X−H distance, θ the H−C to X−C angle and ψ the angle made by the X−H line and the X−C line. The s_j's which appear in the potential functions are then defined in terms of the above-described coordinates by the following relations:

$$s_1=\delta r_1+\delta r_2+\delta r_3, \qquad s_4=\delta r_2-\delta r_3,$$
$$s_2=\delta r_4, \qquad s_5=\delta q_{24}-\delta q_{34},$$
$$s_3=\delta q_{12}+\delta q_{13}+\delta q_{23}, \qquad s_6=\delta q_{12}-\delta q_{13}.$$

The evaluation of the G's in terms of the con-

stants k_1, k_2, k_3, c and k_4 is straight forward and yields the following relations:

$$G_{11}=\tfrac{1}{3}(k_1+8k_2+8k_3); \qquad G_{12}=2\sqrt{2}k_4;$$

$$G_{22}=c; \qquad G_{23}=-\sqrt{3}k_4;$$

$$G_{33}=k_2+k_3; \qquad G_{31}=-\frac{2\sqrt{6}}{3}(k_2+k_3);$$

$$G_{44}=\frac{k_1}{2}+k_2+\frac{(2\sqrt{2}+\cot\psi)^2}{2(2\sqrt{2}\cot\psi-1)^2}k_3;$$

$$G_{45}=-\frac{3}{2}\frac{(2\sqrt{2}+\cot\psi)}{\sin^2\psi(2\sqrt{2}\cot\psi-1)^2}k_3;$$

$$G_{55}=\frac{9}{2}\frac{k_3}{\sin\psi(2\sqrt{2}\cot\psi-1)^2}; \qquad G_{46}=-(\tfrac{3}{2})^{\frac{1}{2}}k_2;$$

$$G_{66}=\tfrac{3}{2}k_2; \qquad G_{56}=0.$$

We may substitute these into the expressions for the P's and R's as given by Rosenthal and Voge[8] and thus obtain the cubic equations for the parallel and perpendicular frequencies in terms of our potential force constants. The coefficients are:

$$R_1=\frac{37}{36}k_1+\frac{11}{9}(k_2+k_3)+\frac{12+M_2}{12M_2}c-\frac{\sqrt{2}}{3}k_4,$$

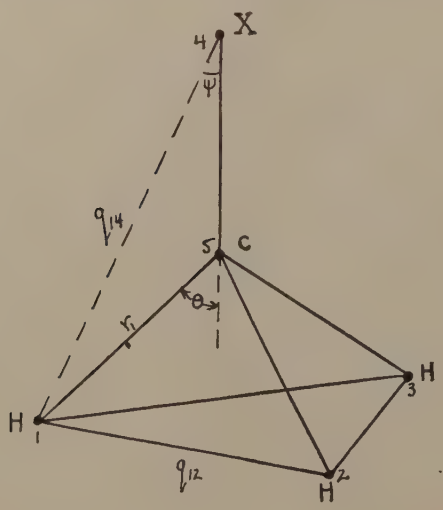

FIG. 2.

[8] J. E. Rosenthal and H. H. Voge, J. Chem. Phys. **4**, 134 (1936).

$$R_2=-\frac{5}{4}k_1(k_2+k_3)+\frac{c}{12M_2}$$
$$\times\left\{\left(\frac{37}{3}+M_2\right)k_1+\left(\frac{44}{3}+M_2\right)(k_2+k_3)\right\}$$
$$-\left(\frac{11}{3M_2}k_4^2+\frac{1}{4}k_4^2+\frac{\sqrt{2}}{3}k_1k_4\right),$$

$$R_3=\frac{c}{12M_2}(15+M_2)k_1(k_2+k_3)-\frac{15+M_2}{4M_2}k_1k_4^2,$$

$$P_1=\frac{1}{9}\left(10k_1+\frac{49}{2}k_2\right)$$
$$+\frac{9-\frac{8}{9}(2\sqrt{2}\sin\psi+\cos\psi)^2+\frac{27}{2M_2}\sin^2\psi}{(2\sqrt{2}\cos\psi-\sin\psi)^2}k_3,$$

$$P_2=\frac{1}{2}\left\{k_1k_2+\frac{2k_3(k_1+2k_2)}{(2\sqrt{2}\cos\psi-\sin\psi)^2}\right.$$
$$\left.+\cos\psi\frac{(2\sqrt{2}\sin\psi+\cos\psi)}{(2\sqrt{2}\cos\psi-\sin\psi)^2}k_2k_3\right\}$$
$$+\frac{3}{2M_2}\frac{\sin^2\psi(k_1+2k_2)k_3}{(2\sqrt{2}\cos\psi-\sin\psi)^2}$$
$$+\frac{27}{2M_2}\frac{\sin^2\psi\left(k_1+\frac{5}{2}k_2\right)k_3}{(2\sqrt{2}\cos\psi-\sin\psi)^2}+k_1k_3+\frac{5}{2}k_1k_2$$
$$-\frac{9}{4}\frac{(2\sqrt{2}\sin\psi+\cos\psi)^2}{(2\sqrt{2}\cos\psi-\sin\psi)^2}k_2k_3$$
$$+\frac{81}{4}\frac{k_2k_3}{(2\sqrt{2}\cos\psi-\sin\psi)^2},$$

$$P_3=\frac{27}{8}\left\{\frac{2}{3}(2\sqrt{2}\cos\psi-\sin\psi)^2\right.$$
$$\left.+\sin^2\psi\left(\frac{12}{M_2}-\frac{2}{3}\right)+\frac{4}{3}\right\}\frac{k_1k_2k_3}{(2\sqrt{2}\cos\psi-\sin\psi)^2}.$$

By assigning observed values to the λ's appearing in these equations we may evaluate the constants.

The values of k_1 and k_2, which are to be chosen so as to best fit the methane frequencies, are evaluated as follows: In the above expressions we

set $M_2=1$, $\psi=\theta/2$, $k_3=k_2$, $c=k_1$ and $k_4=0$, and identify those frequencies which correspond to the parallel frequencies of the ZYX_3 molecule and those that correspond to the perpendicular. The R's and the P's then become:

$$R_1=\tfrac{1}{9}(19k_1+22k_2), \qquad P_1=\tfrac{1}{9}(10k_1+49k_2),$$
$$R_2=\tfrac{1}{9}(10k_1{}^2+46k_1k_2), \qquad P_2=6k_1k_2+(22/3)k_2{}^2,$$
$$R_3=(8/3)k_1{}^2k_2, \qquad P_3=8k_1k_2{}^2.$$

Dennison[9] has shown that the methane frequencies ν_1, ν_3, ν_4 correspond to the parallel frequencies of the ZYX_3 molecule and hence should satisfy Eq. (1), when the proper values of k_1 and k_2 are taken. ν_2, ν_3, ν_4 should come out of Eq. (2), since they correspond to the perpendicular frequencies of the ZYX_3 molecule.

For $k_1=4.878\times10^5$ dynes/centimeter, and $k_2=0.443\times10^5$ dynes/centimeter, we obtain the values given in the Table I. We have also given the experimentally observed values to show what order of approximation is involved when the methane molecule is treated by means of a valence type potential function.

The discrepancy between the observed and calculated normal frequencies of methane may be attributed to two factors. In the first place, the calculated frequencies were obtained by means of a very simple type of potential function, involving only two arbitrary constants, k_1 and k_2. It is very probable that such a picture does not give the exact nature of the binding forces. In the second place, one must consider the anharmonicity corrections. Any calculation of normal frequencies assumes that the atoms of the molecule may be considered as simple harmonic oscillators. For small amplitudes of vibration of these atoms about their positions of equilibrium, this approximation is good, but will become increasingly bad with greater amplitudes. Thus even the most general potential function for methane, involving five arbitrary constants, may not give the normal frequencies of heavy methane within a percent of the observed values.

In evaluating the remaining constants of the methyl halides, that is, k_3, c and k_4, one may notice that only k_1, k_2 and k_3 appear in the expressions for the perpendicular frequencies of these molecules. One chooses k_3 so that equation (2) gives the correct value for ν_6, rather than the other perpendicular frequencies, because it is the most sensitive to the value of k_3. The other two roots of this equation may now be used to check against the other two observed perpendicular frequencies.

[9] D. M. Dennison, Rev. Mod. Phys. **3**, 208 (1931).

TABLE I.

BAND	CALCULATED	OBSERVED
	Parallel Frequencies	
ν_1	2876	2915
ν_3	3050	3014
ν_5	1324	1304
	Perpendicular Frequencies	
ν_2	3050	3014
ν_4	1495	1520
ν_6	1324	1304

Once k_3 is determined, c and k_4 are adjusted to fit ν_5 and ν_3 in Eq. (1). The remaining root is then checked against the remaining observed parallel frequency. In the numerical work we set $m=1$, $M_1=12$ and M_2 equal to the atomic weight of iodine, bromine, chlorine or fluorine as the case may be. For the carbon-halogen distance, x_0, a mean value as given by infra-red and electron diffraction data[10] was used. This distance of course determines the angle ψ, since the dimensions of the methyl group are assumed to be the same as those of methane. It was found that the values of the force constants were not very sensitive to this angle.

ICH_3

Consider the methyl-iodide molecule. Since the binding forces of the methyl group are taken to be those of methane, the dimensions of this group are also taken from methane as given by Johnston and Dennison.[11] Thus r_0, the H−C distance, is 1.11×10^{-8} cm. The total height of this molecule, from the iodine atom to the plane of the three hydrogen atoms, is about 1.75×10^{-8} cm. This value is not very accurate but the force constants are quite insensitive to this dimension.

When these constants are used in Eq. (2) it becomes:

$$\lambda_\perp{}^3-(6.625+1.096k_3)\lambda_\perp{}^2$$
$$+(6.481+7.156k_3)\lambda_\perp-6.714k_3=0,$$

[10] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[11] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

TABLE II.

BAND	CALCULATED	OBSERVED	% DEVIATION
ν_2	3034	3074	1.3
ν_4	1445	1446	0.1
ν_6	886*	886	
ν_1	2916	2916	0.0
ν_3	1252*	1252	
ν_5	532*	532	

a cubic in λ. The constant k_3 may be considered as an adjustable parameter, to be so determined as to give one of the observed frequencies. We do this as follows: The ν_6 fundamental frequency of ICH_3 is 886 waves cm^{-1}. Since we define λ to be $4\pi^2 m c_L^2 \nu^2$ where c_L is the velocity of light, ν the frequency in waves cm^{-1} and m the mass of the hydrogen atom, its value is 0.4641×10^5 dynes/cm. This is inserted into the above cubic equation and the resulting equation is then solved for k_3. The value thus obtained is 0.463×10^5 dynes/cm. If our assumed potential energy function is a correct one, once this constant is determined, the roots of Eq. (2) must then correspond to the three normal perpendicular frequencies of this molecule. In Table II we have tabulated the observed and calculated frequencies. The starred frequencies are those used for the adjustment of our constants, so that they do not serve as checks.

The constants c and k_4, are obtained from Eq. (1). To do this we must use two observed frequencies. ν_5 and ν_3 are observed to be 532 and 1252 waves/cm., respectively. The corresponding λ's are then 0.1671 and 0.9257. When these values are put into Eq. (1) there result two equations in c and k_4, which may be treated simultaneously. It should be noticed that these equations are quadratic in k_4. Upon solving them, one obtains the two values: $k_4=0.786\pm0.134$. The occurrence of two roots is of course due to the mathematical method employed since physically only one such value can be correct. To determine which of these is the appropriate one, one must turn to entirely different considerations. The two values of k_4 will give two different values for c. Since c measures the strength of the bond between the methyl group and the halogen atom, we may get an approximate value for it by assuming that one of the normal frequencies corresponds to the motion of the methyl group against the halogen atom. Sutherland and Dennison[2] have calculated the constant c on such an assumption. Comparison with their results shows that the c corresponding to k_4 equal to 0.652×10^5 dynes/cm is the correct one. The other value comes out to be entirely too high. The value we adopt therefore is 3.292×10^5. With these constants determined one may solve Eq. (1) and obtain the three ν's which correspond to the three parallel normal frequencies. These are tabulated in Table II together with the experimentally observed values.

The agreement between the calculated and observed frequencies is on the whole very satisfactory. One must of course remember that the values which act as checks are not the ones most sensitive to the force constants. Fortunately there is another independent check on the force constants which determine the perpendicular motions. When such constants are known one may calculate the fine structure spacing of these bands and compare them with the experimental results of Bennett and Meyer.[1] This calculation is presented later in this paper.

$BrCH_3$

Next let us consider the methyl bromide molecule. The distance from the bromine atom to the plane of the hydrogen atoms is 2.28×10^{-8} cm. The atomic weight of the bromine atom is taken as 79.92. The cubic equation for the perpendicular frequencies then becomes:

$$\lambda_\perp^3-(6.625+1.111k_3)\lambda_\perp^2+(6.481+7.250k_3)\lambda_\perp-6.816k_3=0.$$

The observed ν_6 for this molecule is 957 cm^{-1} so that $\lambda_6=0.5407\times10^5$. This value of λ gives $k_3=0.536\times10^5$. Putting this into the expression for the parallel bands one obtains:

$$\lambda_\parallel^3-(6.209+0.096c-0.471k_4)\lambda_\parallel^2+(5.966+0.566c-2.299k_4-0.296k_4^2)\lambda_\parallel-0.472c+1.448k_4^2=0.$$

The λ's corresponding to the observed ν_5 and ν_3 are 0.2197 and 1.0072, respectively. The solution of the two simultaneous equations arising from these, again gives two roots for k_4; *viz.* $k_4=0.798\pm0.023$. For reasons already discussed under ICH_3 we chose the smaller value and the corre-

sponding value of c is 4.193. The calculated frequencies as well as the observed ones are listed in Table III.

$ClCH_3$

The fact that the two values of k_4 for $BrCH_3$ are more nearly alike than the two values for ICH_3 does not appear to be purely accidental, as will become apparent when we consider methyl chloride and methyl fluoride.

The chlorine atom is 2.07×10^{-8} cm from the plane of the hydrogen atoms. The atomic weight of chlorine is taken to be 35.4 so that the expression for the perpendicular bands becomes:

$$\lambda_\perp^3-(6.625+1.140k_3)\lambda_\perp^2+(6.481+7.435k_3)\lambda_\perp-7.010k_3=0.$$

From the above equation $k_3=0.5964$ when λ is set equal to 0.6143. With this value for k_3 the expression for the parallel bands becomes:

$$\lambda_\parallel^3-(6.283+0.112c-0.471k_4)\lambda_\parallel^2+(6.337+0.671c-2.299k_4-0.354k_4^2)\lambda-0.601c+1.736k_4^2=0.$$

The observed λ's are $\lambda_3=0.3164$ and $\lambda_5=1.0842$. It turns out that only complex values of k_4 will satisfy the two equations resulting from the two λ's, simultaneously. This of course indicates a flaw in our assumed form of the potential function. It can, however, be readily shown that this flaw is not a serious one. For successive members of this methyl halide series the parabolae which represent the possible values of k_4 lie increasingly higher with respect to the zero axis. Thus in the case of ICH_3 the two roots are further apart than in the case of $BrCH_3$, while for $ClCH_3$ this parabola does not cross the axis at all. We may take the point of nearest approach of the parabola to the axis as the root and see how well such a value of k_4 gives the frequencies. The c corresponding to the real part of $k_4=0.725$

TABLE III.

BAND	CALCULATED	OBSERVED	% DEVIATION
ν_2	3034	3062	0.9
ν_4	1450	1450	0.0
ν_6	957*	957	
ν_1	2915	2917	0.0
ν_3	1306*	1306	
ν_5	610*	610	

TABLE IV.

BAND	CALCULATED	OBSERVED	% DEVIATION
ν_2	3035	3047	0.4
ν_4	1456	1460	0.3
ν_6	1020*	1020	
ν_1	2916	2923	0.3
ν_3	1363	1355	0.7
ν_5	732*	732	

$\pm0.173i$ is 4.417. The calculated ν's are given in Table IV. We take k_4 to be 0.725×10^5.

It is apparent from the above table that even though we get complex roots for k_4, our assumptions cannot be far from the truth. The behavior of the constant k_4 may be ascribed to the two factors already mentioned in the discussion of the methane molecule; namely, that the corrections for anharmonicity are neglected and the fact that the assumed form of the potential energy function is not entirely correct.

FCH_3

As would be expected from the study of ICH_3, $BrCH_3$ and $ClCH_3$, the parabola for the possible values of k_4 of FCH_3 will approach the zero axis less closely than in the case of $ClCH_3$. This turns out to be the case. To fix the constant k_3 we have taken 1.75×10^{-8} cm to be distance of the fluorine atom from the plane of the hydrogen atoms. The atomic weight used was 19.00. With $\lambda_6=0.8504$ corresponding to the observed ν_6 of 1200 cm^{-1} the expression:

$$\lambda_\perp^3-(6.625+1.213k_3)\lambda_\perp^2+(6.481+7.905k_3)\lambda_\perp-7.495k_3=0$$

gives $k_3=0.8097\times10^5$.

The expression for the parallel frequencies:

$$\lambda_\parallel^3-(6.544+0.136c-0.471k_4)\lambda_\parallel^2+(7.637+0.855c-2.299k_4-0.443k_4^2)\lambda_\parallel-0.911c+2.182k_4^2=0$$

will give two equations in k_4 and c when λ is set successively equal to 0.6495 and 1.2865 corresponding to the observed ν_5 and ν_3, respectively. Solving these simultaneously for k_4, one obtains the complex values $0.713\pm0.344i$. Assigning to k_4 its real part, 0.713, c comes out to be 6.091. In Table V appear the frequencies calculated with these constants.

TABLE V.

BAND	CALCULATED	OBSERVED	% DEVIATION
ν_2	3037	2987	1.7
ν_4	1489	1476	1.0
ν_6	1200*	1200	
ν_1	2917	2914	0.1
ν_3	1517	1476	2.8
ν_5	1049*	1049	

FINE STRUCTURE OF THE PERPENDICULAR BANDS*

The perpendicular bands of the methyl halides show the usual anomalous fine structure that is found in the axially symmetrical molecules such as NH_3 and spherically symmetrical molecules such as methane. This anomaly arises from the interaction of the degenerate vibratory motions and the angular momenta of the molecule.

Johnston and Dennison[11] have shown how the vibration-rotation interaction may be calculated when the dimensions and the force constants of the molecule are known. Following their method we shall calculate the fine structure spacing of the perpendicular bands of ICH_3, $BrCH_3$, $ClCH_3$, and FCH_3, using the force constants obtained above.

That the perpendicular frequencies of axially symmetrical molecules are doubly degenerate is evident from the fact that the molecular forces are isotropic in a plane perpendicular to the axis of symmetry.

A proper choice of phases and amplitudes of two such harmonic vibrations at right angles to each other will give a circular motion. The angular momentum vector of this rotation is clearly in the direction of the symmetry axis. Each atom contributes to this internal angular momentum as it vibrates about its position of equilibrium. The total contribution may therefore be written as

$$M_2(x_5\dot{y}_5-\dot{x}_5y_5)+M_1(x_4\dot{y}_4-\dot{x}_4y_4)+3m(x_{123}\dot{y}_{123}-\dot{x}_{123}y_{123})-3m(\xi\dot{\eta}-\dot{\xi}\eta). \quad (3)$$

The first three terms are the respective angular momenta of the halogen atom, the carbon atom and the center of gravity of the hydrogen atoms about the axis of symmetry. The last term represents the sum of the angular momenta of each hydrogen atom about an axis through its equilibrium position and parallel to the symmetry axis. The negative sign that precedes this term is due to the fact that the angular momenta of the hydrogen atoms is opposite in direction to that of Z, Y and G. (See Johnston and Dennison.[11])

The eigenvalues for the above expression are readily obtained when it is expressed in terms of normal coordinates, since then the wave functions are the usual Hermitian polynomials.

The relation between the coordinates used in the expression (3) and the normal coordinates Q_2, Q_4, $\cdots$ etc. are

$$x_5=(\rho_{51}A_2+\rho_{52}D_2)Q_2+(\rho_{51}A_4+\rho_{52}D_4)Q_4+(\rho_{51}A_6+\rho_{52}D_6)Q_6,$$

$$x_4=(\rho_{41}A_2+\rho_{42}D_2)Q_2+(\rho_{41}A_4+\rho_{42}D_4)Q_4+(\rho_{41}A_6+\rho_{42}D_6)Q_6,$$

$$x_{123}=(\rho_{31}A_2+\rho_{32}D_2)Q_2+(\rho_{31}A_4+\rho_{32}D_4)Q_4+(\rho_{31}A_6+\rho_{32}D_6)Q_6,$$

with identical expressions for y_5, y_4, and y_{123}, except that Q_2, Q_4 and Q_6 are replaced by R_2, R_4 and R_6, normal coordinates perpendicular to Q_2, Q_4 and Q_6, respectively. A_2, A_4, $A_6\cdots D_6$ have already been given explicitly in the preceding paper. The ρ's are defined as follows:

$$\rho_{51}=\frac{[((3m+M_1)/2)C_0+3mM_1b_0^2]}{A_0(3m+M_1+M_2)},$$

$$\rho_{52}=\frac{[((3m+M_1)/2)a_0C_0/b_0-M_2C_0/2]}{A_0(3m+M_1+M_2)},$$

$$\rho_{41}=\frac{M_2(3a_0b_0m+C_0/2)}{A_0(3m+M_1+M_2)},$$

$$\rho_{42}=\frac{(a_0M_2/b_0-M_2-3m)C_0/2}{A_0(3m+M_1+M_2)},$$

$$\rho_{31}=\frac{M_2(a_0b_0M_1-b_0^2M_1-C_0/2)}{A_0(3m+M_1+M_2)},$$

$$\rho_{32}=\frac{(M_1+a_0M_2/b_0)C_0/2}{A_0(3m+M_1+M_2)}.$$

* A calculation of the ζ's for the methyl halides was made somewhat earlier by Professors W. F. Colby and David M. Dennison using slightly different coordinates. Their formulae, which were not published, are in agreement with ours and we wish to make acknowledgment of this earlier calculation.

TABLE VI.

α	FCH_3	$ClCH_3$	$BrCH_3$	ICH_3
α	0.79	0.38	0.27	0.19
β	16.32	14.05	13.40	12.62
γ	2.83	2.79	2.81	2.81
δ	2.60	1.56	1.24	0.98
ϵ	−0.188	−0.112	−0.090	−0.071
φ	2.28	2.44	2.49	2.55

TABLE VII.

	$\Delta\nu_2$		$\Delta\nu_4$		$\Delta\nu_6$	
	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.
FCH_3	6.9	7.5	12.0	11.5	5.5	5.6
$ClCH_3$	7.7	8.2	12.9	12.0	6.4	7.0
$BrCH_3$	8.0	9.0	13.2	11.9	6.9	7.4
ICH_3	8.1	9.0	13.2	11.8	7.2	7.7

In terms of the normal coordinates, expression (3) becomes

$$\sum_i (Q_i\dot{R}_i-\dot{Q}_iR_i)\{A_i^2(M_2\rho_{51}^2+M_1\rho_{41}^2+3m\rho_{31}^2)$$
$$+2A_iD_i(M_2\rho_{51}\rho_{52}+M_1\rho_{41}\rho_{42}+3m\rho_{31}\rho_{32})$$
$$+D_i^2(M_2\rho_{52}^2+M_1\rho_{42}^2+3m\rho_{32}^2)-3mB_i^2\}.$$

Since the wave functions are the well-known Hermitian orthogonal functions, the eigenvalues $\hbar\zeta$ for the first excited states of the bands ν_i are immediately given by

$$A_i^2(M_2\rho_{51}^2+M_1\rho_{41}^2+3m\rho_{31}^2)$$
$$+2A_iD_i(M_2\rho_{51}\rho_{52}+M_1\rho_{41}\rho_{42}+3m\rho_{31}\rho_{32})$$
$$+D_i^2(M_2\rho_{52}^2+M_1\rho_{42}^2+3m\rho_{32}^2)-3mB_i^2.$$

Johnston and Dennison have derived the expression for the fine structure spacing $\Delta\nu_i$ in terms of the ζ's. They give it as (in waves per cm):

$$\Delta\nu_i=\frac{\hbar}{c_L}\left(\frac{1-\zeta_i}{C_0}-\frac{1}{A_0}\right).$$

To obtain numerical values for the above, one must have the general force constants α, β, γ, δ, ϵ, and φ, which may be readily obtained from the valence type force constants k_1, k_2 and k_3 already discussed in the earlier part of this paper. The transformation equations are:

$$\alpha=\frac{3r_0^2k_3}{2(a_0-b_0)^2}, \qquad \delta=\frac{4r_0k_3}{a_0-b_0},$$

$$\beta=\frac{4}{3}(k_1+2k_2+8k_3), \qquad \epsilon=-\frac{1}{2\sqrt{3}}\frac{r_0k_3}{a_0-b_0},$$

$$\gamma=\frac{4}{9}\left(k_1+\frac{25}{2}k_2+\frac{1}{2}k_3\right), \qquad \varphi=\frac{4}{3\sqrt{3}}\left(k_1-\frac{5}{2}k_2-k_3\right),$$

and from these one obtains for the general force constants the values given in Table VI.

In comparing the observed and calculated $\Delta\nu$'s (Table VII), actual differences rather than percentages should be considered because the spacings are small quantities both numerically and experimentally. The experimental values are taken from the work of Bennett and Meyer and are the mean values of about fifteen to twenty lines. The individual spacings vary considerably so that these values are to be considered good only within a few tenths of a wave per cm. Though there seems to be a systematic deviation of the calculated values from the observed, we feel that they are small enough to indicate that the force constants are very nearly correct. Of course, the fine structure spacing of these perpendicular bands depends only on the force constants which enter into the perpendicular frequencies so that they act as a check on k_1, k_2, and k_3 only.

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